Stability of High-Level Waste Forms
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RESEARCH OBJECTIVE: The objective of the proposed effort is to use a new approach to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility. The effort will also yield thermodynamic values for waste components that are fundamentally required for corrosion models used to predict the leaching/corrosion behavior for waste glass and spent fuel material. This basic information and understanding of chemical behavior can subsequently be used directly in computational models of leaching and transport in geologic media, in designing and engineering waste forms and barrier systems, and in prediction of chemical interactions.

RESEARCH PROGRESS AND IMPLICATIONS: The ASM development has continued through a number of phases. During the first phase, two of the main ternary systems were modeled and the model was shown to out perform other published models for the same systems (Na_2O-B_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2). In the second phase of the project, the five component system that makes-up the backbone of typical waste glass melts was modeled (Na_2O-CaO-Al_2O_3-B_2O_3-SiO_2).

The addition of components to the ASM becomes increasingly more complex as the total number of components in the model increases. The model expansion requires a significant amount of experimental work and model optimization. The progress on the third project phase, includes:

- the fabrication and measurement of over 100 unique multi-component melt compositions (Hanni et al. 2005)

- the development of a binary FeO_x-MnO_x phase diagram (Crum et al. 2005)
- development of experimental techniques and measurement of both CrO_x and SO_x in multi-component glass melts (Hrma et al. 2004 and 2005)
- the testing of Bi_2O_3 solubility in typical Hanford high-level waste glasses (Tran et al. 2006)
- refinement of the Na_2O-Al_2O_3-B_2O_3-SiO_2 database
- assessment of sulfur solubility

Experimental Efforts

The impacts of this testing includes a solid contribution to the understanding of multi-component silicate melt chemistry and thermodynamics as evidenced by the publications listed below. The testing work on Cr_2O_3 solubility in waste glass melts led to the development of a high Cr waste glass melt (=2 wt% as Cr_2O_3). The results of this melt have led to a change in the Hanford waste cleanup system planning and have cut an estimated 35% of the projected high-level waste glass volume to be produced at Hanford.

Na_2O-Al_2O_3-B_2O_3-SiO_2 Quaternary System

The previous database for the above system could reproduce the best binary and ternary phase diagram information available in the literature. The ternary Na_2O-Al_2O_3-SiO_2 system was reproduced better than was possible using any other known database. A few precipitation experiments on nepheline ($NaAlSiO_4$) plus B_2O_3 and on ($NaAlSiO_4$ + x SiO_2) plus B_2O_3 gave significantly lower precipitation temperatures than we obtained from modeling calculations. rechecking the experimental results found the data to be reproducible. Checking our data for B_2O_3-containing binary and ternary systems against what was available in the literature did not reveal discrepancies, but the amount of data in the literature is sparse.

With little experimental data to use, it was believed that strong liquid interactions between borate species and those in liquid Na_2O-Al_2O_3-SiO_2 species could readily explain the disagreement (more careful thermochemical studies of borate systems should reveal the influence of such interactions). Some reasonable complex liquid associate species ($NaAlSiO_4$ plus B_2O_3 and $NaAlSi_2O_6$ plus B_2O_3) were created along with thermodynamic information using techniques described in earlier papers, and it became possible to accurately reproduce the experimental data. However, the database must be reliable for all compositions in the Na_2O-Al_2O_3-B_2O_3-SiO_2 quaternary system, so a careful reassessment of all subsystems that included B_2O_3 as a component was necessary.

The Na_2O-B_2O_3 phase diagram and thermodynamic information was thoroughly examined, with a special focus on reported Na_2O activity measurements in glass solutions in the system. Excellent overall agreement was obtained between the literature information and that calculated using our newly revised database. Small differences that occur between reported and calculated activity data in the very B_2O_3-rich region (>94% B_2O_3) of the diagram are a result of theoretical inconsistencies between reported phase equilibria (liquidus and immiscibility data) and activity data. Both sets of information cannot be reproduced exactly using reasonable thermodynamic data in our database.

The ternary Na_2O-B_2O_3-SiO_2 system was re-assessed, using a new nepheline-type $NaBSiO_4$(s,l) species in the dataset. Without such a species, the experimental phase diagram results could not be reproduced. Such a nepheline-type boria containing solid phase has been reported, but not confirmed in the literature. The $NaBSiO_4$(s) species is only slightly more stable than a mixture of ($NaBO_2$ + SiO_2); i.e. the formation reaction of ($NaBO_2$ + SiO_2 = $NaBSiO_4$) has a very small negative free energy, and $NaBSiO_4$(s) melts at a low temperature. Using a liquid associate species of $NaBSiO_4$(l) in our database allows for an accurate calculation of the metastable ternary immiscibility reported for the Na_2O-B_2O_3-SiO_2 system.

Sulfate Solubility

Efforts were made to reproduce experimentally determined sulfur solubilities reported in earlier work at PNNL. An associate species model by the authors that successfully provided sulfur behavior trends in commercial glasses was applied to the compositions of current waste streams. The results did not reproduce the experimental trends. Alternatively, a sulfur solubility model usable at low concentrations that was provided by Thermfact, Ltd was also applied to the data. Again the trends could not be reproduced, which do logically follow the alkali metal content of the melts. It is suspected that the relatively low sulfur concentrations (single mole percents) either are not accurately known, or the compositions of interest are not yet adequately modeled.

INFORMATION ACCESS:

PUBLICATIONS

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WEBSITE

www.ca.sandia.gov/HiTempThermo/index.html